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Chemical effects in the Kβ X-ray emission spectra of sulfur

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Abstract

In this work our previous study about chemical effects in the Kα spectra of S compounds employing high-resolution X-ray spectroscopy has been extended to the Kβ emission spectra. The measurements were performed with a wavelength dispersive single crystal spectrometer operated in the von Hamos geometry having an energy resolution comparable to the natural linewidth of the measured Kβ X-ray lines. The target fluorescence was produced by irradiating the samples with the bremsstrahlung from an X-ray tube. The energies and widths of the main components in the Kβ emission spectrum are given for different sulfur compounds (sulfide, sulfite, sulfate). The measured energy shifts between the Kβ lines of the compounds and elemental sulfur are presented as a function of the sulfur oxidation state and compared with the results obtained from the former Kα measurements.

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1. Introduction

Besides the determination of elemental concentrations, analytical techniques based on the observation of the sample X-ray emission can also be efficiently used for the chemical speciation of elements in the sample. In such chemical speciation measurements, the use of high energy-resolution instruments like crystal spectrometers is, however, mandatory. Chemical speciation can be based on the measurements of the changes in the integrated intensity of different satellite lines relative to the diagram line as it has been done recently for several manganese compounds [1]. In this case a middle energy resolution (around 10 eV) is sufficient. Another method is to determine the chemical shifts of the characteristic X-ray emission lines and the changes of their lineshapes but in this case a higher energy resolution (below 1 eV) is required. Gohshi and coworkers [2,3] were the first to report quantitative chemical state analysis of S, Cr and Sn based on the energy shifts of the characteristic X-ray emission lines. In this work a double crystal spectrometer was used in order to obtain the needed energy resolution of a few tenths of eV. Similarly, a double crystal spectrometer in combination with an X-ray tube has been developed by Konishi et al. [4] to perform chemical state analysis of low Z elements. Single crystal spectrometers, however, can also be used in chemical speciation measurements based on the energy shifts of the characteristic X-ray emission lines. In a recent work [5,6], we have indeed shown that using a Johansson type single crystal spectrometer we were able to reach an energy resolution below the natural linewidth of the Kα diagram lines and to get reliable chemical speciations of the measured sulfur compounds from the sole energy shifts of the S Kα line. A systematic and nearly linear dependence of the

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observed energy shifts on the sulfur oxidation state was found in these measurements.

Compared to the Kα diagram line, which corresponds to the core–core ($1s \rightarrow 2p$) transition, more pronounced chemical effects can be observed in the Kβ emission since the Kβ transition directly involves valence electrons which are strongly affected by the chemical environment of the atom. In the present paper we have therefore extended our previous chemical effect study to the Kβ emission spectra of sulfur. Whereas in our previous work proton excitation was used, an X-ray tube was employed in the present measurements. Since the Kβ line is much weaker than the Kα one (for sulfur, $I(K\beta)/I(K\alpha) \cong 0.031$ [7]), relatively high beam-currents would be needed in case of charged particle excitation to record well resolved Kβ spectra. This may then result in a significant temperature rise of the sample during the measurements leading to thermal deformations or even permanent damages of the irradiated target. Since such problems are not encountered with the X-ray fluorescence method, the sulfur Kβ spectra were measured using the bremsstrahlung from an X-ray tube for the sample irradiation.

In this work a single crystal spectrometer operated in the von Hamos geometry has been used to measure the photoinduced S Kβ X-ray spectra emitted from different sulfur compounds. For each measured sample the absolute energies and widths of the main components were determined. The energy shifts between the Kβ lines of the compounds and elemental sulfur are presented as a function of the sulfur oxidation state and compared with the shifts obtained previously from measurements of the Kα spectra of the same samples.

2. Experiment and data analysis

The measurements of the photoinduced Kβ X-ray spectra of sulfur were performed at the University of Fribourg using a high-resolution crystal X-ray spectrometer in the von Hamos geometry [8]. The S targets (S, FeS, Na_2SO_3, Na_2SO_4, $(NH_4)_2SO_4$), in the form of pellets prepared from fine powders, were irradiated with the bremsstrahlung of a Cr X-ray tube operated at 20 kV and 10 mA. The Coolidge-type X-ray tube was mounted vertically and oriented in such a way that the axis of the bremsstrahlung emission cone was horizontal and perpendicular to the dispersion axis of the spectrometer. As a result of this set-up and the partial polarization of the bremsstrahlung emitted by X-ray tubes, the intensity of the vertically-polarized component of the bremsstrahlung impinging on the samples was estimated to be about 20% bigger than the horizontally-polarized one. Since the anisotropy parameter characterizing the angular distribution of the fluorescence radiation after ionization of an atom by linearly polarized photons is expected to vanish for the 1s shell [12] the measured Kβ fluorescence X-ray emission should not depend on the emission angle as it has been confirmed by a variety of experiments (see, e.g. [13]). In order to avoid any possible contamination of the spectrometer vacuum chamber the target pellets were additionally covered with 12 μm kapton foil which together with relatively low X-ray tube power used in our measurements resulted in low counting rate so several hours were needed to record a single spectrum. The photons emitted from the S targets were reflected in first order by a $SiO_2(1\,\bar{1}\,0)$ crystal ($2d = 8.5096$ Å) cylindrically curved to a radius of 254 mm. The diffracted photons were detected by a back-illuminated charged coupled device (CCD) detector. The latter, which was thermoelectrically cooled down to −50 °C, consists of 1340×400 pixels with a pixel resolution of $20 \times 20\ \mu m^2$. In each image good pixel events were sorted out by setting energy windows corresponding to the Kβ photons of interest. The filtered images were then added and their sum projected on the dispersion axis of the spectrometer. The so-obtained position spectra were calibrated in energy using the position of the $K\alpha_1$ line from the pure S target which served as a reference. A value of 2307.885 eV was adopted for the energy of the reference line [9]. The measured Kα spectrum from pure S target was also used for the determination of the instrumental response function. Typical Kβ spectra measured with the pure sulfur, sulfide, sulfite and sulfate targets are presented in Fig. 1.

In the modified von Hamos slit geometry used in the present experiment, the target is viewed by the crystal through a narrow rectangular slit. The latter which defines the effective source width is usually the main source of the instrumental broadening. In our measurements a slit width of ~0.2 mm corresponding to a broadening of 0.7 eV was chosen. The actual instrumental resolution was determined by fitting the $K\alpha_{1,2}$ reference spectrum. The latter could be fitted very well with two 1.25 eV wide Lorentzians. Taking into account the natural linewidths of the $K\alpha_{1,2}$ transitions (0.61 eV each [10]), an instrumental broadening of 0.64 eV was obtained in good agreement with the estimated value due to the above-mentioned finite slit width. The shape of the spectrometer response was found to be well described by a Lorentzian function. Except for FeS and elemental S, the measured Kβ spectra were fitted with several Lorentzians. For illustration the fitted spectrum of the Na_2SO_3 target is presented in Fig. 2. The FeS spectrum exhibiting a single broad peak, was fitted with a single Voigt function corresponding to the convolution of the observed nearly-Gaussian profile with the Lorentzian instrumental response. For the case of elemental S, MO calculations [11] reveal three main components so that the measured spectrum was fitted with three lines, two Lorentzians and one Voigtian. The width of the Lorentzian components in the Voigt profiles used in the fits of the FeS and S spectra was kept fixed at the value corresponding to the instrumental broadening.

3. Results and discussion

In our previous work concerning the sulfur Kα emission spectra [5,6], it was shown that the characteristic Kα diagram lines of the sulfur compounds were shifted in energy,

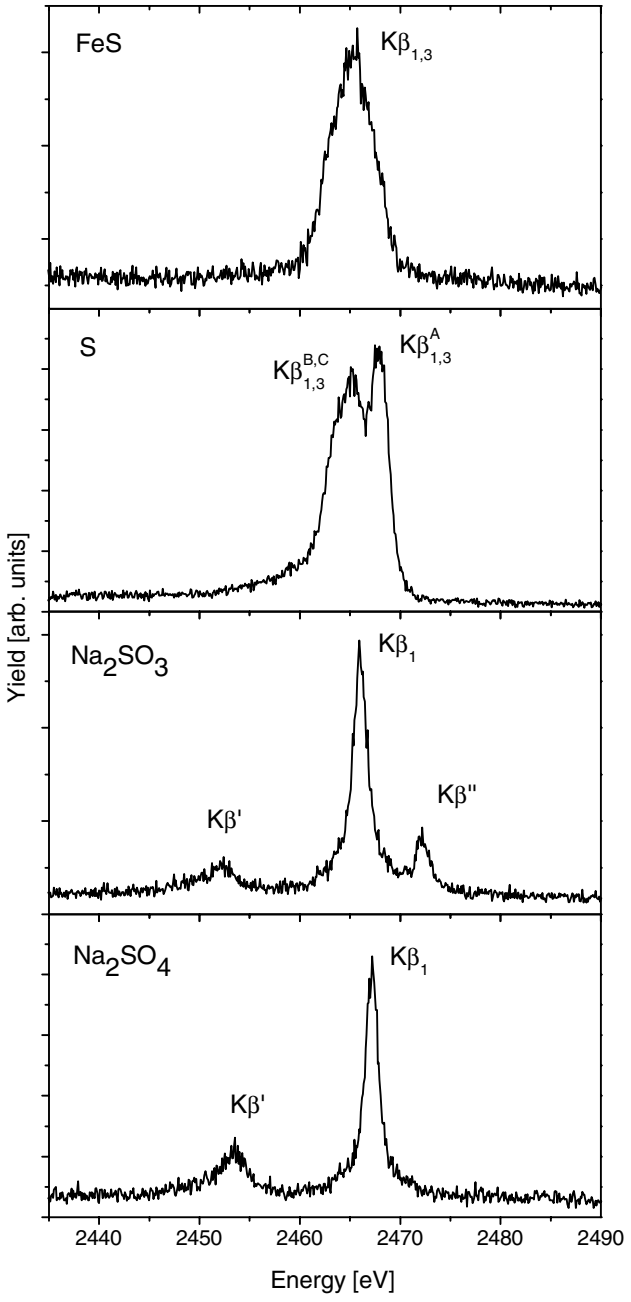

Fig. 1. High-resolution photoinduced S Kβ X-ray emission spectra measured for sulfide, pure sulfur, sulfite and sulfate compound targets. The pronounced changes of the spectral structures as well as the energy shifts of the main components reflect the influence of the chemical environment of the sulfur atoms in different compounds.

the size of the shift depending on the sulfur oxidation state. The shape of the spectrum, however, was not affected by the chemical environment of the sulfur atoms, conserving its typical $K\alpha_{1,2}$ doublet structure for each compound. For the case of the Kβ emission spectra, similar energy shifts related to the oxidation state of sulfur are observed. As expected and already observed (for example [11] and references therein) our measurements also confirmed strong differences in the spectra shapes of the different compounds (Fig. 1) containing several partly overlapping lines

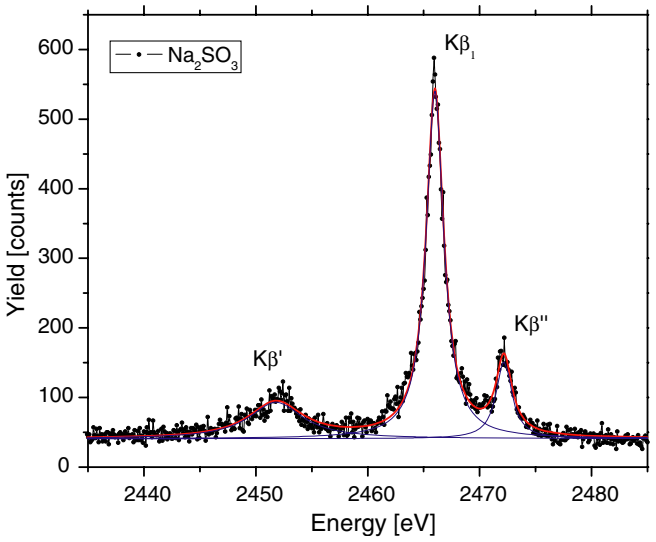

Fig. 2. The measured spectrum of the Na_2SO_3 target fitted with three Lorentzian profiles as described in the text.

originating from transitions from the valence band in the case of the Kβ emission spectra. As shown in Fig. 1, the S Kβ X-ray emission spectra of compounds containing sulfur–oxygen bonds consist of a main line, usually denoted $K\beta_1$, and an additional low energy satellite line (Kβ′). In certain cases, such as in $[SO_3]^{2-}$ compounds, a high energy satellite line (Kβ″) is also observed. In order to interpret theoretically the shapes of the measured lines, results of molecular orbital (MO) calculations are usually used. In the paper of Uda et al. [11], in which the MO calculations were performed using the discrete variational (DV)-Xα method, it was shown that the main peaks in the S Kβ spectra from compounds containing S–O bonds originate from molecular orbitals involving mainly oxygen 2p and 2s orbitals and sulfur 3p and 3s orbitals. Such theoretical investigations of the shapes of the observed S Kβ spectra are, however, beyond the scope of the present work whose main goal is to probe the dependence of some relatively simple spectral characteristics (energies and linewidths of the main components) on the oxidation state of sulfur in the different measured compounds.

The energies and linewidths of the $K\beta_1$, Kβ′ and Kβ″ components for the measured sulfur compounds containing sulfur–oxygen bonds are presented in Table 1. The energies and linewidths obtained for the three S components and the broad FeS peak are also reported. The errors of the absolute energies listed in Table 1 originate from the fitting procedure and the uncertainty on the crystal-detector distance which is needed for the energy calibration of the spectrometer. Tabulated linewidths have been corrected for the instrumental broadening described with the 0.64 eV wide Lorentzian. Quoted uncertainties for the linewidths are due to fitting errors only. The same holds for the energy shifts reported in Fig. 3.

From Table 1 one can see that the signs of the energy shift of the Kβ line are the same as the ones observed for

Table 1
Energies and widths of the main components in the measured Kβ emission spectra

	Target	Kβ′		Kβ$_1$		Kβ″	
		Energy (eV)	FWHM (eV)	Energy (eV)	FWHM (eV)	Energy (eV)	FWHM (eV)
S^{4+}	Na_2SO_3	2451.80 ± 0.16	5.21 ± 0.39	2466.01 ± 0.10	1.28 ± 0.02	2472.18 ± 0.11	1.07 ± 0.09
S^{6+}	Na_2SO_4	2453.24 ± 0.12	3.34 ± 0.19	2467.17 ± 0.10	0.98 ± 0.02	–	–
	$(NH_4)_2SO_4$	2453.04 ± 0.12	4.15 ± 0.18	2467.29 ± 0.10	1.31 ± 0.02	–	–
		Kβ$_{1,3}$					
		Energy (eV)	FWHM (eV)				
S^{2-}	FeS	2465.17 ± 0.10	4.94 ± 0.04				
		$K\beta'^{C}_{1,3}$		$K\beta^{B}_{1,3}$		$K\beta'^{A}_{1,3}$	
		Energy (eV)	FWHM (eV)	Energy (eV)	FWHM (eV)	Energy (eV)	FWHM (eV)
S	Pure S	2463.69 ± 0.12	2.74 ± 0.11	2465.48 ± 0.11	1.74 ± 0.17	2467.96 ± 0.10	1.65 ± 0.04

Quoted widths were already corrected for the experimental broadening.

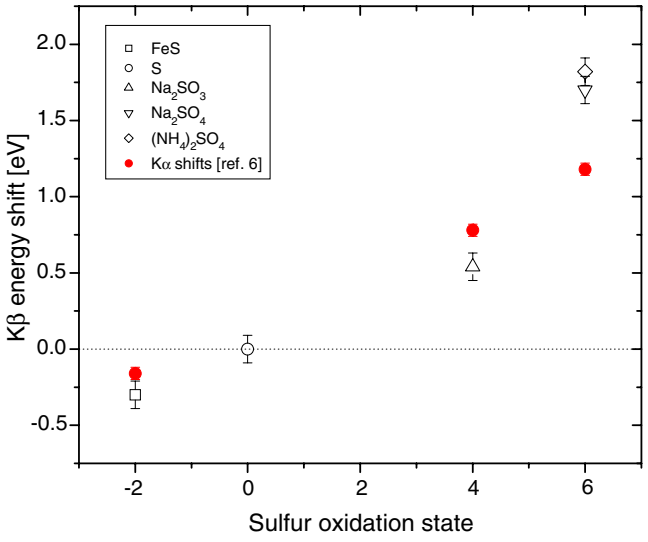

Fig. 3. Energy shifts relative to the Kβ line weighted average energy corresponding to the pure S target measured for different sulfur compounds as a function of the sulfur oxidation state (open symbols). For comparison the previously measured [6] energy shifts of the Kα line (solid circles) are also plotted in the figure.

the Kα transition. However, whereas an energy difference of 0.40 ± 0.06 eV was found between the Kα lines of $[SO_3]^{2-}$ and $[SO_4]^{2-}$ compounds [6], an average energy difference of 1.22 ± 0.06 eV is observed for the Kβ$_1$ line. We have therefore tried to use the measured chemical shifts as a quantitative criteria for the oxidation state of sulfur in the measured samples. Since in the case of compounds with SO bonds the sharp Kβ$_1$ peak dominates the spectrum we have taken the energy of this particular line for the calculation of the energy shifts. For the FeS and S samples, the centroid energy of the broad peak and the weighted average energy of the three peaks used in the fit were considered, respectively. The measured energy shifts relative to the Kβ line weighted average energy corresponding to the pure S target are plotted in Fig. 3 as a function of the sulfur oxidation state (open symbols). For comparison the previously obtained shifts relative to the Kα line of pure S target [6] are also presented in the Figure (solid circles). As shown, the measured energy shift increases as a function of the sulfur oxidation state. The observed increase is similar to the one observed with the Kα line, at least for oxidation states up to S^{4+}. According to this observation one can conclude that chemical speciation of sulfur in the case of low oxidation states can be derived more advantageously from measurements of the energy shifts of the Kα line since the latter is much more intense than the Kβ one and chemical energy shifts of Kα and Kβ transitions are comparable. In addition the quasi-independence of the Kα spectrum shape on the oxidation state makes the analysis and energy shift determination easier and more reliable. Furthermore, the relatively simple profile of the Kα spectrum enables to determine the mass ratio of different compounds in mixed targets as it was demonstrated in [5]. However, going to higher oxidation states, the energy shift is significantly bigger for the Kβ transition so that in such cases Kβ line measurements present a good potential for analytical purposes especially when spectrometer with a slightly lower energy resolution in the order of 1–2 eV is used. For example such a moderate resolution should be still sufficient to distinguish between $[SO_3]^{2-}$ and $[SO_4]^{2-}$ compounds but only if Kβ transitions are used.

4. Summary and conclusion

Sulfur compounds are among the most important pollutants emitted into the atmosphere. The determination of the oxidation state of sulfur is of prime importance since it determines its chemical reactivity. It is therefore necessary to study and further develop analytical methods for chemical speciation. In this work the photoinduced Kβ X-ray emission of different S compounds was measured with a Bragg type single crystal spectrometer. The energy resolution of our measurements was comparable to the natural linewidth of the measured lines. Precise energies and natural linewidths of the main components that could be resolved within the measured spectra are given.

A systematic dependence of the Kβ line energy shift as a function of the sulfur oxidation state similar to the one previously found in Kα line measurements was observed for sulfur oxidation states up to S^{4+}. For higher oxidation states a more pronounced dependence was evinced by our measurements demonstrating the possibility to perform reliable sulfur chemical speciation on the basis of Kβ line energy measurements providing that the experimental energy resolution is in the range of 1–2 eV.

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